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Annual Progress Report

The Growth of Gallium Nitride Films via the Innovative Technique of Atomic Layer Epitaxy

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Table of Contents

List of Figures.....	iii
List of Tables	v
1. Introduction.....	1
1.1 Properties and Applications.....	1
1.2 Limitations.....	2
2. Nitrogen Sources.....	3
2.1 "Straight-Through" Microwave Plasma Source.....	3
2.2 Electron Cyclotron Resonance (ECR) Plasma Source.....	4
3. Growth Results	6
3.1 Gallium Nitride	6
3.2 Aluminum Nitride and AlN/GaN Layered Structures.....	8
3.3 Boron Nitride and BGaN Graded Layers.....	12
4. Future Research.....	15
4.1 Nitrogen Source.....	15
4.2 Solid Solution Materials.....	16
5. Analysis System	17
6. Related Activities.....	17
7. References.....	19
A. Distribution List—Annual Report.....	21



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List of Figures

1. Proposed optical devices which can be made using selected compositions from the In-Ga-Al-N solid solution series to tailor properties such as bandgap and/or lattice parameter to the specifics of an application..... 2
2. Schematic diagram of the glass nitrogen glow discharge source. The microwave applicator is not shown..... 4
3. Cross-sectional diagram of the head of the ECR plasma source designed, fabricated and commissioned at NCSU. This source is mounted on the MBE source flange in the location of a normal effusion cell. 5
4. Shape of the magnetic lens at different current values (left), and dependence of the extracted species (ion flux) on magnetic field density ratio of both magnets (right)..... 5
5. X-ray diffraction pattern from GaN thin film ($a_0=4.508 \text{ \AA}$). 7
6. Cathodoluminescence spectrum of a 3000 \AA thick cubic GaN film on (100) β -SiC taken at 15K with electron beam of 20 mA at 5 kV. Main peak is at 3.30 eV..... 8
7. Time sequence RHEED photographs of the growth of cubic AlN and GaN heterostructures on β -SiC monitored in two different directions..... 9
8. Two sets of RHEED patterns which show a 30° rotation of the overgrowth with respect to the substrate (sapphire) in the directions $\langle 01\bar{1}0 \rangle$ and $\langle 2\bar{1}\bar{1}0 \rangle$ 10
9. Auger depth profile of GaN/AlN heterostructure on sapphire. (Note, that Y scale represents raw intensity and not relative concentration.)..... 11
10. Cross-section TEM micrograph. Note the presence of the five AlN/GaN double layers (each single layer $\sim 50\text{--}60 \text{ \AA}$ thick). 12
11. Back plan-view TEM micrograph of GaN/BN layer. Note signs of tearing in lower left region, indirectly indicating the presence of multiple layers of BGaN. 14
12. Auger electron spectroscopy scan of the untreated surface of the BN film. 14

13. Auger electron spectroscopy sputtered depth profile of a BN/BGaN/GaN/ β -SiC film. Note peak in nitrogen trace as interface of BN is passed. 15
14. Diagram showing the relationship between lattice parameter and bandgap in the hexagonal structure solid solution series of GaN/AlN/InN. 17

List of Tables

1. Range of conditions used in GaN thin film growth.....	6
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1. Introduction

1.1 Properties and Applications

Gallium nitride (GaN) is a III-V compound semiconductor having a direct, wide bandgap (3.5 eV at 300K) as well as a large saturated electron drift velocity. This unique combination of properties coupled with appropriate doping provides the potential for fabrication of short wavelength semiconductor lasers, LEDs and detectors as well as transit-time-limited (IMPATT, etc.) microwave power amplifiers from this material. In addition, aluminum nitride (AlN) and indium nitride (InN), are direct bandgap materials of 1.95 eV and 6.28 eV, respectively. These other nitrides form a solid solution series with GaN, which will permit bandgap and lattice parameter engineering in order to fabricate the devices already mentioned. The current research directly addresses this problem via the use of MBE and the related technique of atomic layer epitaxy, substrate temperatures $\leq 700^{\circ}\text{C}$, and atomic nitrogen sources.

The present growth method involves the deposition of gallium (and/or aluminum or indium) from a standard effusion cell and nitrogen from a remote microwave electron cyclotron resonance (ECR) plasma onto a substrate (whose temperature is considerably lower than that required for CVD). This ECR nitrogen source was designed and constructed in-house for our MBE system, resulting in a more compact source which allowed the source to be much closer to the substrate than would have been possible with a commercially available system. It has been demonstrated that the higher reactivity of the nitrogen atoms will result in a more complete incorporation of nitrogen into the GaN films with the corresponding increase in growth rate and reduction of excess nitrogen vacancies. This approach will make possible the kind of devices shown in Figure 1, where several different nitrides and their solid solutions are used to engineer a device with very specific properties.

This program has also been unique in the growth of the cubic phase of several of these nitrides, specifically GaN and AlN. The cubic phase of these materials has even better performance potential when made into devices. Theoretically, cubic GaN (and AlN) have an even higher saturated electron drift velocity which would increase its potential for high frequency applications. As such, the near term anticipated payoff is the first successful growth of GaN films and the associated range of solid solutions, which will allow the fabrication of a host of electronic and short wavelength optoelectronic devices noted above.

InGaN - n	lattice matched
$\text{Al}_x\text{In}_{1-x}\text{N}$	active layer
AlInN - p	graded layer
AlN - p	buffer layer
SiC - p	

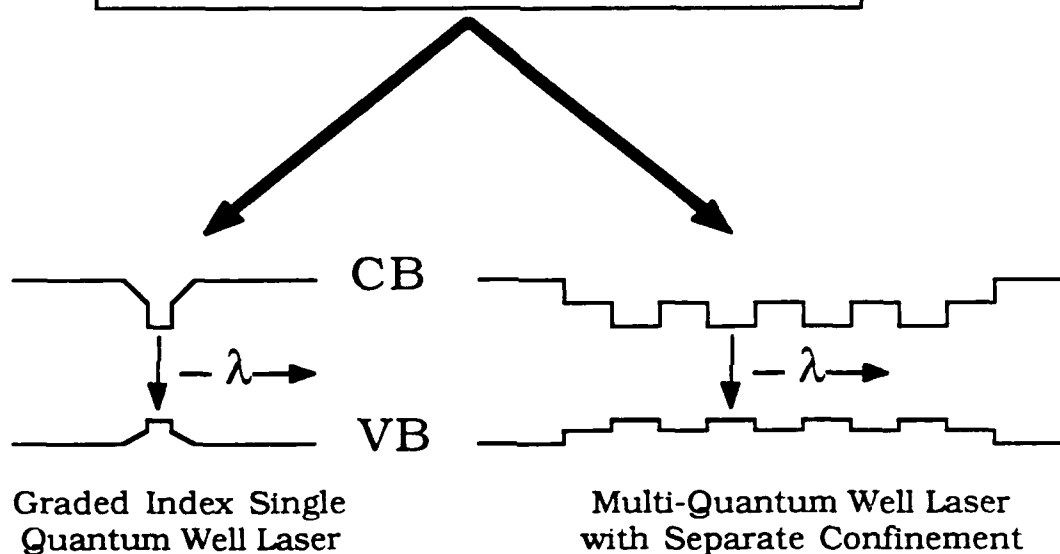


Figure 1. Proposed optical devices which can be made using selected compositions from the In-Ga-Al-N solid solution series to tailor properties such as bandgap and/or lattice parameter to the specifics of an application.

1.2 Limitations

Utilization of GaN has been very limited to date because all material produced has possessed an intrinsic n-type carrier concentration of at least 10^{17} cm^{-3} and normally in the range of 10^{18} – 10^{19} cm^{-3} . The only high resistivity single crystal material produced has required compensation with a p-type dopant (usually Zn). However, this approach greatly reduces the electron mobility in the film. In addition, intentional growth of p-type GaN has never been achieved, and so devices requiring growth p-n junctions cannot be produced. (All diode struc-

tures produced to date have been metal-insulator-semiconductor (MIS) structures.)

It is a nearly universal consensus that the n-type character is caused by N vacancies produced during the growth process. The basis for this reasoning is that GaN decomposes at $\approx 1123\text{K}$ at a N_2 pressure of 1 atm. The equilibrium vapor pressure of N_2 over GaN at 1323K (a common growth temperature used in chemical vapor deposition (CVD) growth of GaN) is 100 atm. Thus molecular nitrogen is not used as a source in CVD growth of GaN. A commonly used nitrogen source in CVD growth is ammonia (NH_3). The equilibrium vapor pressure of NH_3 over GaN at 1323K is only 650 Pa,[1] thus allowing the GaN to form at those elevated temperatures. Further discussion of the limitations of GaN growth is covered in detail by Davis *et al.*[2] and the reader is referred to this publication for more information.

2. Nitrogen Sources

As mentioned above, the most common source of nitrogen for growth of GaN has been ammonia with hydrazine and certain azides used much less frequently. Since semiconductor grade purities of these materials are nearly impossible to obtain, it was decided to begin work using molecular nitrogen as a source. The nitrogen source finally selected was that obtained from the boiloff from a liquid nitrogen dewar which was subsequently passed through a heated copper gas purifying furnace*. After passing through a regulating UHV leak valve† which also provided positive shut off, the nitrogen gas traveled into one of the sources described below. The choice of microwave frequencies for the excitation source was based on data which showed microwave frequencies more suitable for the dissociation of nitrogen.[3]

2.1 "Straight-Through" Microwave Plasma Source

A small microwave power supply* (100 W max) and its associated applicator cavity** were attached to a glass source designed to work with the applicator cavity. The microwave cavity and its glass enclosure were designed specifically for production of plasmas in flowing gases at reduced pressures.[4, 5]

* Model 2B-20-Q, Centorr Associates, Inc., Suncook, NH 03275

† Series 203 Variable Leak, Granville-Phillips Co., Boulder, CO 80303-1398 or
Model 951 Variable Leak Valve, Varian Vacuum Products Division, Palo Alto, CA

* Model MPG-4, Opthos Industries, Inc., Rockville, MD 20855.

** McCarroll-type, Opthos Industries, Inc., Rockville, MD 20855.

The cavity was a two-piece design, thus it was possible to design the chamber where 100% of the nitrogen passed directly through the plasma discharge. The design of the source is shown in Figure 2. Initial operation showed that it produced a strong nitrogen plasma after ignition with a small Tesla coil (part of normal operation).

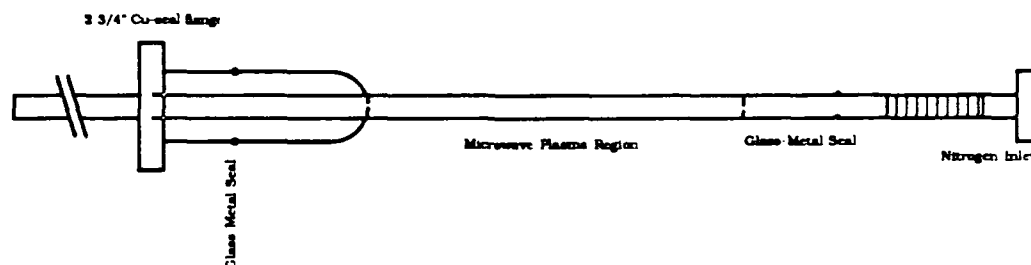


Figure 2. Schematic diagram of the glass nitrogen glow discharge source. The microwave applicator is not shown.

This source was effective at producing nitrogen radicals and other non- N_2 species which promoted the growth of GaN thin films. However, the concentrations of these reactive species at the growth surface were low. As such a growth rate of only $\approx 200 \text{ \AA/h}$ was achieved. The low concentrations of N species was caused by wall recombination effects,[6] due to presence of the orifice and the long tube through which the nitrogen must pass, before reaching the substrate. This wall recombination resulted in the loss of a large percentage of the radicals, etc., produced in the discharge, thus the growth rate was greatly reduced.

2.2 Electron Cyclotron Resonance (ECR) Plasma Source

Due to the aforementioned problems, a major effort was undertaken to design, develop, and construct an in-house microwave ECR source. This source has the potential for greatly enhancing the radical production as well as reducing the wall recombination losses because it can operate at pressures used in standard MBE processes (i.e., 10^{-6} – 10^{-3} Torr) without the need for an orifice or differential pumping. A schematic diagram of the ECR source is shown in Figure 3. The source consists of the same microwave unit for power input as was used previously that feeds its power into a plasma chamber which is surrounded by two solenoid electromagnets. These magnets produce a lens-like magnetic field with a peak value of $\approx 1000 \text{ G}$. Plots of the distribution of the magnetic field are shown in Figure 4.

This magnetic field serves to increase the energy absorption of the electrons in the plasma which provides two benefits. It increases the

electron energy and density in the plasma which aids in the dissociation of strongly bonded molecules like nitrogen. The increased electron density permits the source to operate efficiently at lower pressures ($\approx 10^{-3-6}$ Torr), making it more compatible with MBE growth techniques.

The source mounts on the MBE source flange in the place of a normal effusion cell. The source is of such a novel compact design, that it fits down inside the cryoshroud of the source flange, which reduces the source-substrate distance from ≈ 20 in down to ≈ 8 in. This further increases the active nitrogen flux over commercially available designs by reducing wall recombination losses.

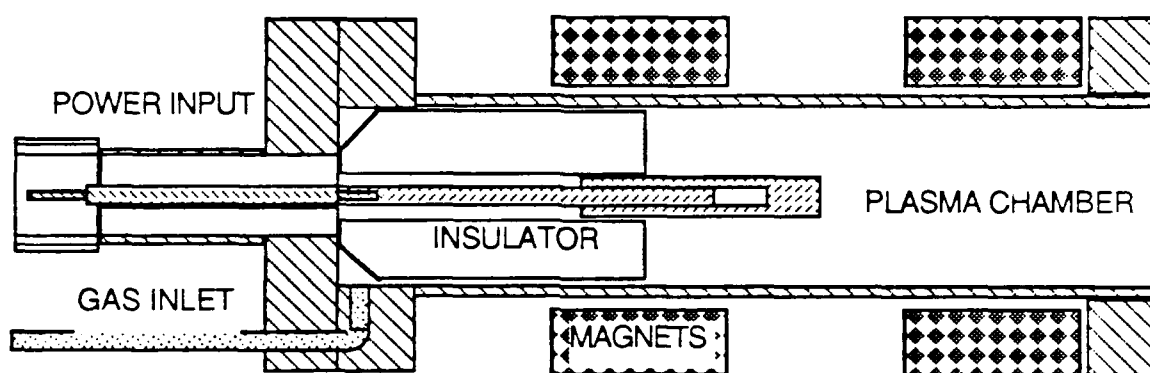


Figure 3. Cross-sectional diagram of the head of the ECR plasma source designed, fabricated and commissioned at NCSU. This source is mounted on the MBE source flange in the location of a normal effusion cell.

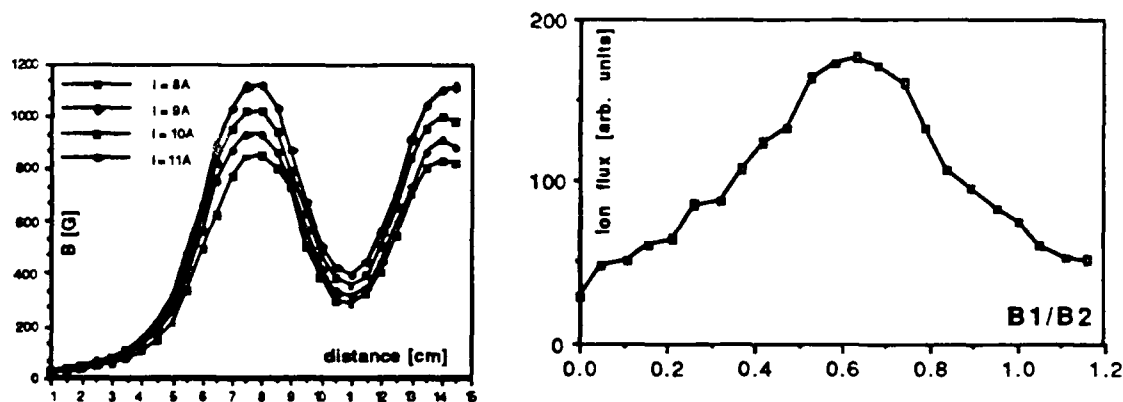


Figure 4. Shape of the magnetic lens at different current values (left), and dependence of the extracted species (ion flux) on magnetic field density ratio of both magnets (right).

The new nitrogen source has been tested, and installed into the existing MBE system. Results indicate about 4-5 times higher flux of active nitrogen species, which resulted in a increased growth rate of nitride thin films ($\approx 900\text{--}1000 \text{ \AA/hr}$). The production and extraction of active species strongly depends on input power, gas pressure, and density and shape of magnetic field.

3. Growth Results

3.1 Gallium Nitride

Up to $0.5 \mu\text{m}$ thick GaN thin films have been grown on sapphire and $\beta\text{-SiC}$, using the more efficient ECR nitrogen source. The structure is wurtzite on sapphire and zinc blende on $\beta\text{-SiC}$. Films show good crystallinity. Electrical properties have been improved by almost two orders of magnitude, again due to the higher nitrogen flux available from the new nitrogen source. The highest resistivity attained to date in the undoped GaN was $\approx 0.5 \Omega\text{-cm}$. The typical range of conditions used during the growth of these films is shown in Table 1.

Table 1. Range of conditions used in GaN thin film growth.

Nitrogen pressure	$5 \times 10^{-6} - 8 \times 10^{-5} \text{ Torr}$
Microwave power	2 - 100 W
Gallium temperature	800 - 950°C
Substrate temperature	500 - 700°C
Growth time	120 - 480 min.
Film thickness	0.05 - 0.5 μm
Electrical resistivity	$\approx 0.008 - 0.5 \Omega\text{-cm}$

X-ray diffraction was performed on a thin film sample of cubic GaN grown at NCSU to determine more accurately the lattice parameter for this material which had previously been reported to be 4.54 \AA , [7] 4.51 \AA , [8] and $4.52\text{--}5 \text{ \AA}$, [9] This pattern resulted in a lattice parameter determination of $a_0 = 4.508 \text{ \AA}$. This diffraction pattern also proves epitaxial growth, as indicated by parallel $\langle 200 \rangle$ directions of the film and substrate (if they were not, the same low index peaks of the film and substrate would not be visible).

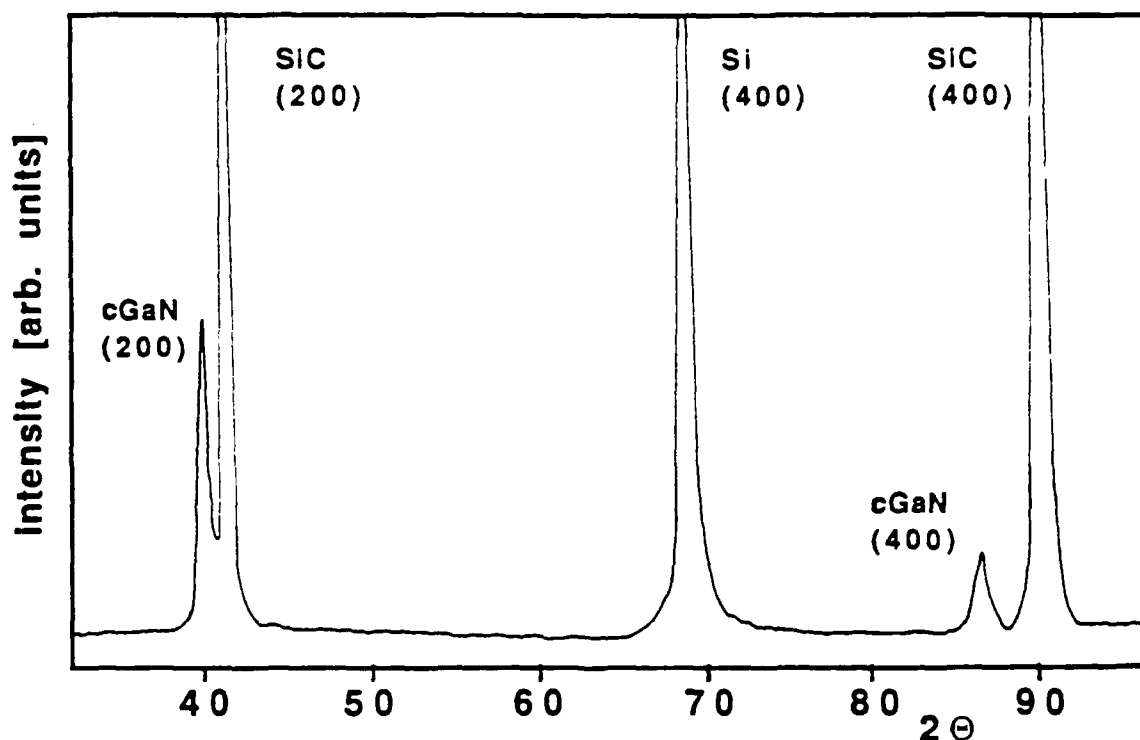


Figure 5. X-ray diffraction pattern from GaN thin film ($a_0=4.508 \text{ \AA}$).

Bandgap calculations for cubic GaN have been reported by Pankove and Bloom.[10] The calculations used a composite of factors known for hexagonal GaN and factors for other cubic semiconductors such as GaAs. The calculations resulted in a value of 3.4 eV, a value essentially unchanged from that of hexagonal GaN. It is a somewhat surprising result, given the bandgap difference for cubic and hexagonal forms of SiC which is considered an analogous material.

Photoluminescent (PL) spectra were taken on both phases (cubic and hexagonal) of GaN grown at NCSU. The bandgap determined from the PL data of the hexagonal material agrees with previously reported values (3.44 eV at room temperature), while the bandgap of cubic GaN shows considerably lower value; ~3.26 eV at room temperature and 3.31 eV at 80K. The PL peaks were quite broad (due mostly to a film thickness effect, because the broadening increases with thinner films); ~300 Å or ~0.13 eV. Thus GaN acts similarly to SiC, as was expected, in that the bandgap for the cubic phase is less than that for the hexagonal phase. In order to determine completely the PL character, thicker films must and will be grown. Below is shown a related cathodoluminescence (CL) spectra (taken by W. J. Choyke at University of Pittsburgh) of a cubic GaN film on a β -SiC substrate. The

main peak here is located at 3.30 eV at 15K and thus correlates well with the PL data taken at NCSU.

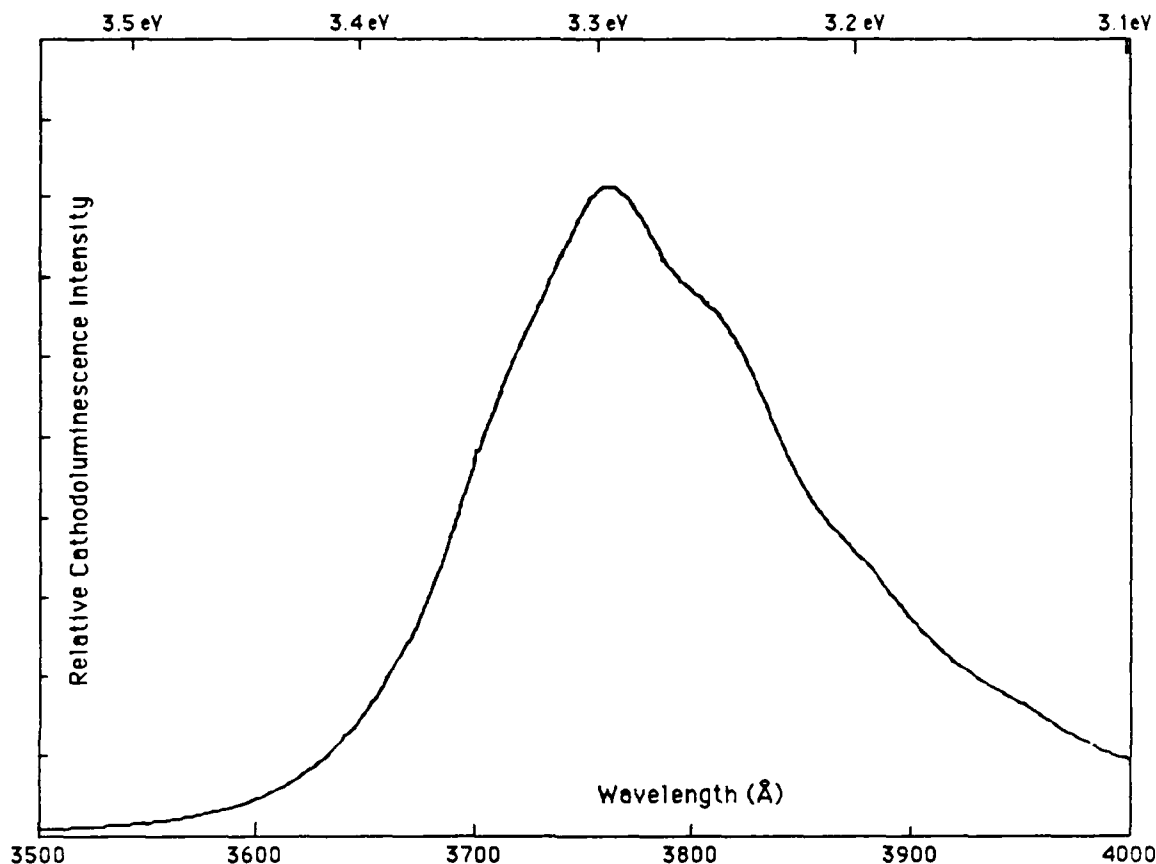


Figure 6. Cathodoluminescence spectrum of a 3000 Å thick cubic GaN film on (100) β -SiC taken at 15K with electron beam of 20 μ A at 5 kV. Main peak is at 3.30 eV.

3.2 Aluminum Nitride and AlN/GaN Layered Structures

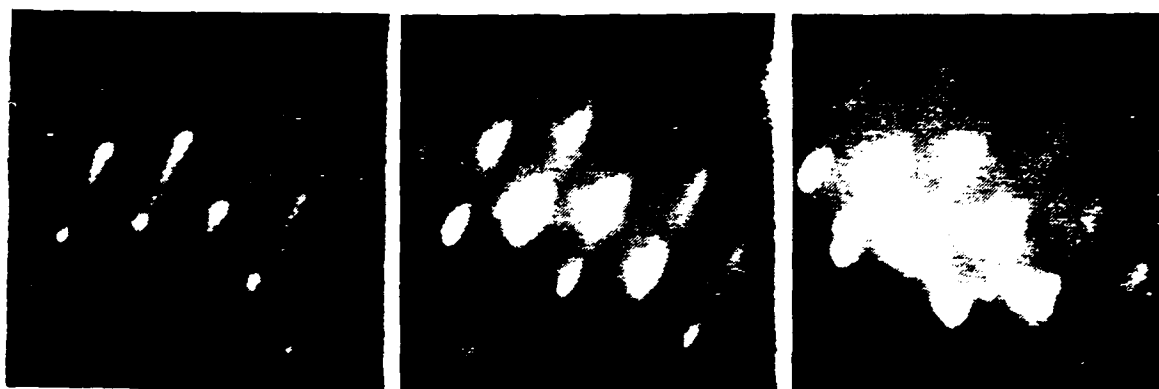
Thin films of aluminum nitride were grown on silicon and sapphire. Material grown on silicon was polycrystalline, while AlN on sapphire showed good crystallinity (wurtzite). This was particularly true when a thin layer of GaN was used as buffer layer at low growth temperatures (5-600°C). The as grown material is highly resistive.

To our knowledge we have grown the first heterostructures of aluminum nitride and gallium nitride on sapphire and the first heterostructures of cubic AlN/GaN on β -SiC. RHEED analysis confirmed good crystallinity and smooth growth throughout the structure. RHEED also showed good crystallinity of the thin cubic AlN layers on cubic GaN, while thicker layers appeared to be heavily twinned. This

can be seen in the following two figures which are time sequence RHEED photographs taken during deposition.

Figure 7 shows the sequence of the growth of AlN on cubic GaN monitored in two different directions. The first pattern in each row shows the GaN before growth of AlN. The second pattern in the first row indicates the rough start of the cubic phase of AlN, which becomes faulted (twins and stacking faults) as film grows thicker—additional spots at the one-third distance visible on the last two patterns in each row.

Zone axis: $\langle 110 \rangle$



700 Å of GaN

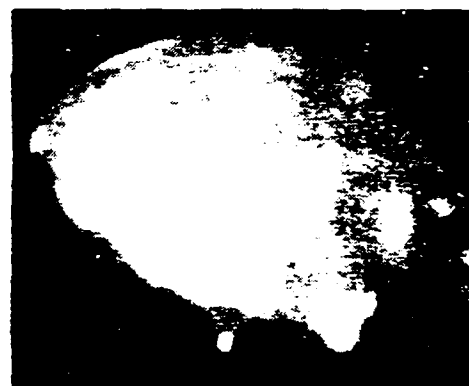
100 Å of AlN

600 Å of AlN

Zone axis: $\langle 100 \rangle$



700 Å of GaN



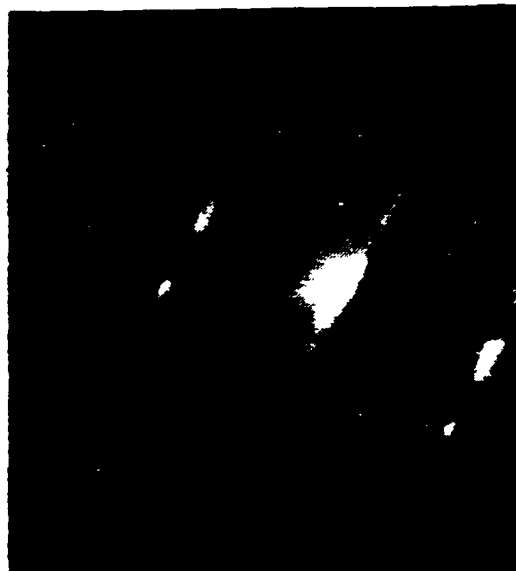
800 Å of AlN

Figure 7. Time sequence RHEED photographs of the growth of cubic AlN and GaN heterostructures on β -SiC monitored in two different directions.

Figure 8 shows the two sets of RHEED patterns show rotation of the overgrowth with respect to the substrate (sapphire). The rotation is 30° , and so the $\langle 2\bar{1}10 \rangle$ direction of substrate becomes parallel to the $\langle 01\bar{1}0 \rangle$ direction of the film (GaN or AlN) and vice versa.



sapphire: $\langle 2\bar{1}10 \rangle$



GaN: $\langle 01\bar{1}0 \rangle$
(30° rotation)



sapphire: $\langle 01\bar{1}0 \rangle$



GaN: $\langle 2\bar{1}10 \rangle$
(30° rotation)

Figure 8. Two sets of RHEED patterns which show a 30° rotation of the overgrowth with respect to the substrate (sapphire) in the directions $\langle 01\bar{1}0 \rangle$ and $\langle 2\bar{1}10 \rangle$.

Auger depth profiles show well defined interfaces for thicker layers. The same is expected also for layers thinner than 100 Å, but it can not be confirmed by Auger spectroscopy. This is because the escape depth for Auger electrons is about 40 Å and also because the depth resolution of the sputtering process is in the same range. Figure 9 shows a depth profile of a multi-quantum well structure of about 50 Å thick layers of AlN and GaN, but unfortunately, due to the lack of resolution of the analytical technique, this figure does not clearly show the interfaces.

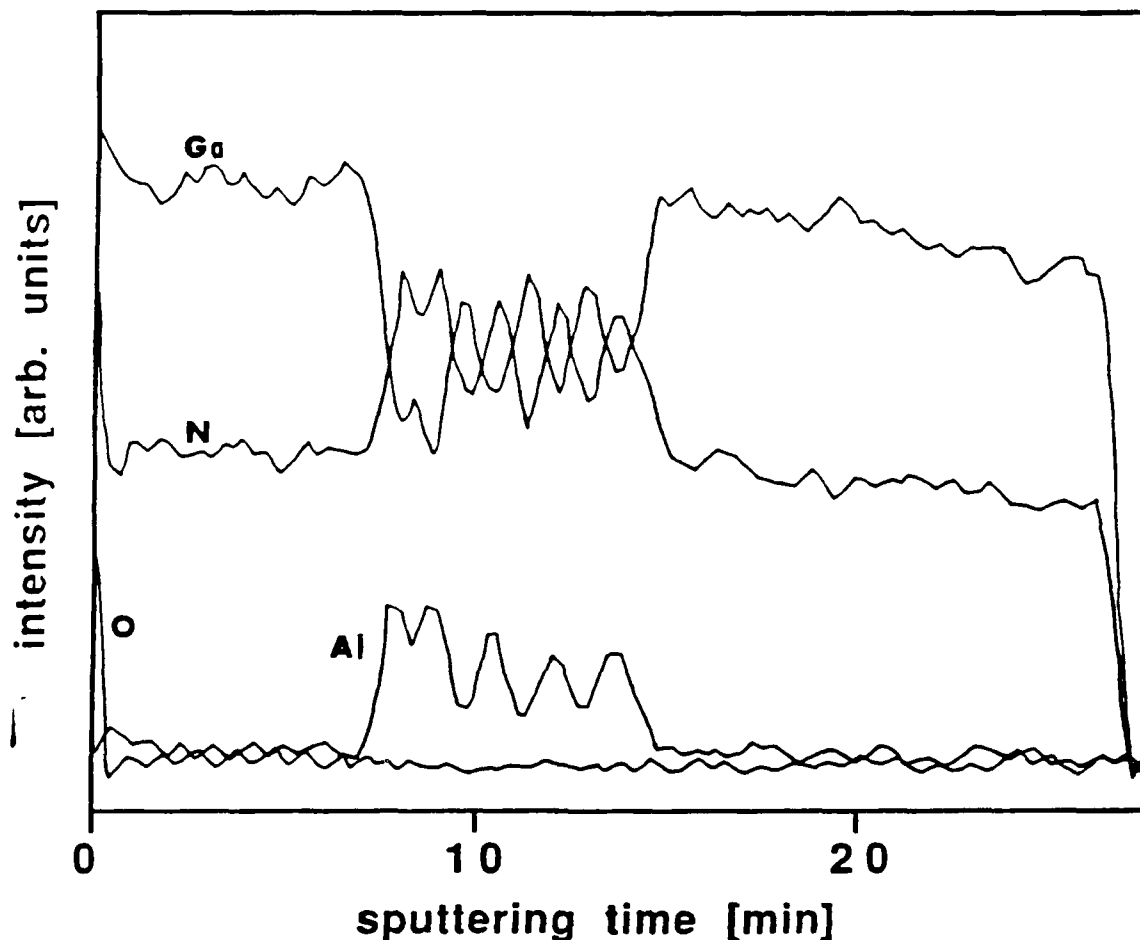


Figure 9. Auger depth profile of GaN/AlN heterostructure on sapphire. (Note, that Y scale represents raw intensity and not relative concentration.)

Cross-section TEM samples were prepared using standard techniques[11] from these multilayer heterostructures. Below is a micrograph from one of these structures. Note the presence of the five AlN/GaN double layers (each single layer ≈ 50 – 60 Å thick). The layers look wavy because of nonuniform TEM sample thickness, which is an

artifact of the ion milling process. This can be seen on the big wave, approximately one-third the figure width from the left, in a well defined narrow black area.



Figure 10. Cross-section TEM micrograph. Note the presence of the five AlN/GaN double layers (each single layer $\approx 50\text{--}60$ Å thick).

3.3 Boron Nitride and BGaN Graded Layers

Growth of cubic boron nitride films has been attempted using a newly designed commercial high temperature effusion cell. This cell is capable of operation at over 2000°C , which should be more than sufficient to evaporate elemental boron. Earlier attempts at using solid boric acid as a source as has been reported[12] in silicon growth were unsuccessful, as the volatility of the boric acid interfered with the operation of the vacuum system.

Growth of boron nitride thin films were also attempted on GaAs (100), Al_2O_3 (10 $\bar{1}$ 0), Ge (100), and Si (100) substrates. RHEED evaluations seem to indicate the films are polycrystalline, but it is unknown at present if they are cubic or hexagonal or a mixture of the two phases. Since the films were polycrystalline in nature, further work with those substrate materials will not continue.

The major obstacle to growth of single crystal films of cubic BN is the small lattice parameter ($a_0=3.62$ Å), which makes finding an appropri-

ate substrate material difficult. The substrates listed above were chosen as an attempt to get a multiple of BN cells to match with the substrate. Since these attempts were unsuccessful, another approach was taken to compensate for the large change in lattice parameter ($\approx 20\%$ smaller than GaN) and perhaps maintain the single crystal structure of the substrate. New growths were attempted which involved deposition of a GaN buffer layer, then grading the composition from pure GaN through to BN. It is thought since the crystal structure of the substrate is the same as is desired in the film, and since the two materials are chemically similar (both being nitrides), the cubic structure might be maintained through to the growing film.

The graded layers were grown on sapphire and β -SiC substrates, which resulted in layers having hexagonal and cubic structure respectively. The crystal structure of the BN films on top of the graded layer remains unclear at this time, but they are not polycrystalline. The following three figures below show the GaN/BN layer from a plan view TEM sample, and an Auger survey scan and depth profile. The TEM photograph shows some evidence of tearing in the sample, which is indirect evidence that there are multiple layers present in the film. Since the BN layer was quite thin (50-100 Å), XTEM was not attempted to determine the structure of the uppermost layers.

The Auger results indicate that a very thin BN layer was deposited on the GaN underlayer, with a small amount of oxygen apparently coming from the boron source. It is unclear if this is due to boron oxide on the surface of the boron charge, or from some other source. A small peak appears in the nitrogen scan as the BN/BGaN interface is crossed. It can also be seen that the graded layer was quite thin, on the order of 2-300 Å. This is considered at present to be too thin for the 20% mismatch to be incorporated into this layer.

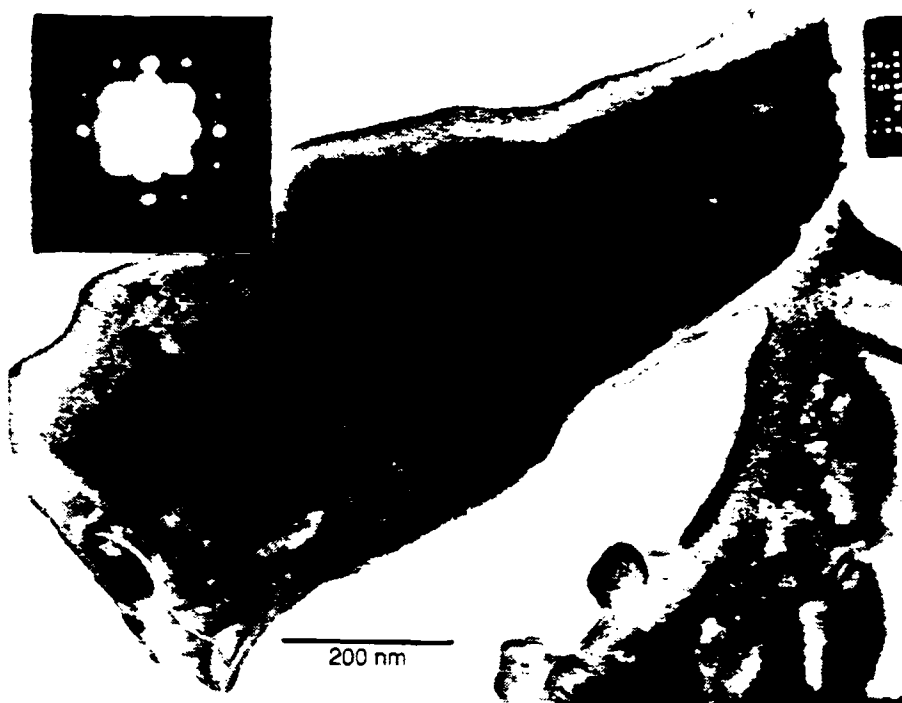


Figure 11. Back plan-view TEM micrograph of GaN/BN layer. Note signs of tearing in lower left region, indirectly indicating the presence of multiple layers of BGaN.

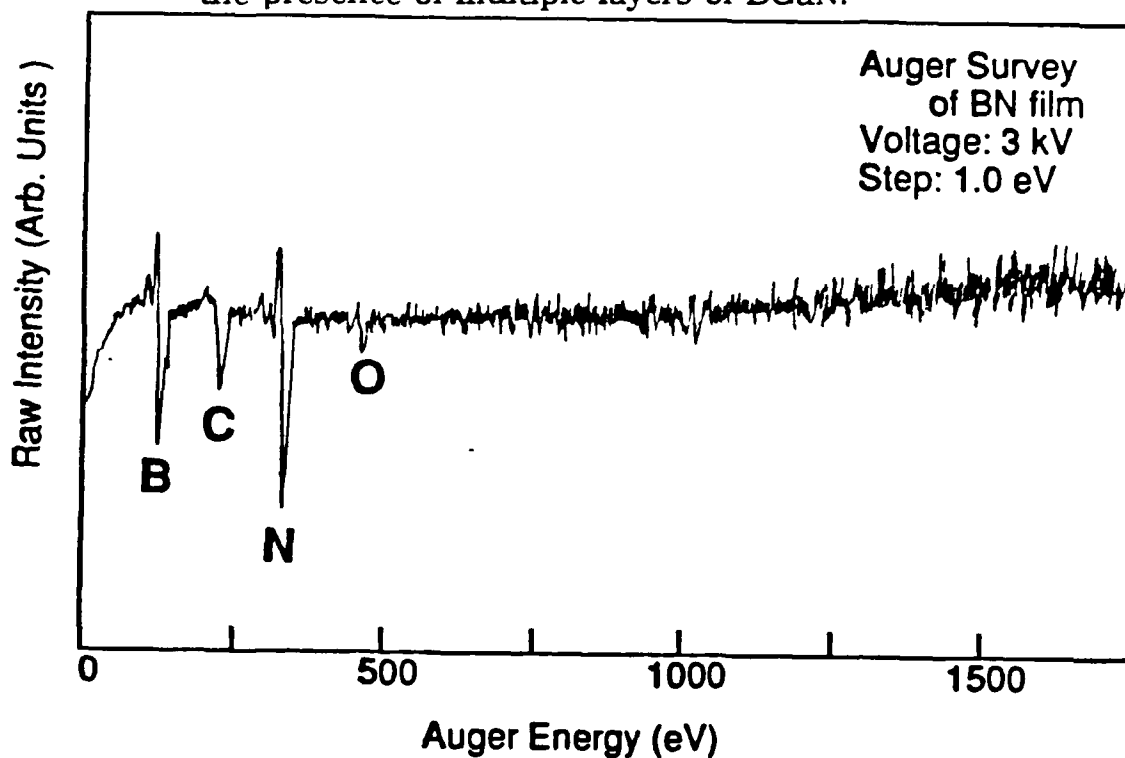


Figure 12. Auger electron spectroscopy scan of the untreated surface of the BN film.

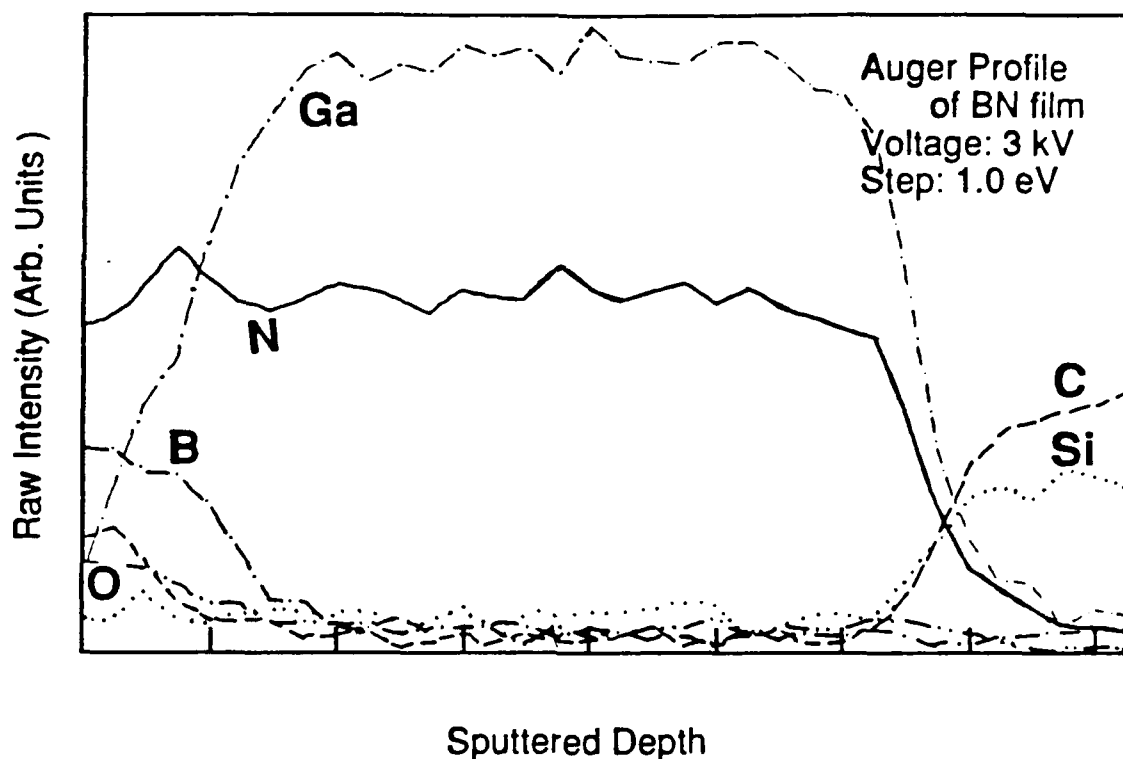


Figure 13. Auger electron spectroscopy sputtered depth profile of a BN/BGaN/GaN/ β -SiC film. Note peak in nitrogen trace as interface of BN is passed.

4. Future Research

4.1 Nitrogen Source

There are several options being investigated to enhance the production of plasma-derived active nitrogen. One such option involves the use of Ar or He metastables to provide additional energy transfer in and downstream from the plasma. Since these metastables are quite long-lived, it is believed to provide improved efficiency of the source. Another such option involves the use of hydrogen/nitrogen mixtures as hydrogen has been cited as a catalyst for nitrogen dissociation.[5] And finally, along with the nitrogen mixtures (which include forming gas, a nitrogen/hydrogen mixture that simulates ammonia), the use of ammonia (NH_3) and hydrazine (N_2H_4) activated in the ECR plasma will be investigated.

The use of hydrogen/nitrogen mixtures will also permit the study of the effect of atomic hydrogen on the reduction of dangling bonds at the growth interface.[13] This reduction could potentially have a

strong positive impact on the resistivity of the resulting films. This capability will also permit the study of hydrogen plasma cleaning of the substrates, to remove the remaining native oxide observed previously[7] from the surface of the substrate. It is believed that this remaining native oxide is responsible for many of the microtwin-type defects observed at the interface.

4.2 Solid Solution Materials

There is great potential in the growth of solid solutions of these nitrides for tailoring bandgap and/or lattice parameter for the desired application. In the case of AlInN the bandgap is in the range of 2–6.3 eV, and for AlGaIn the range is 3.4–6.3 eV. With these two binary solid solutions, structures can be grown which are lattice matched, yet have different bandgaps, a necessary ingredient for many optical devices. Deposition of the ternary solid solution of AlGaInN further enlarges the bandgap range. The third binary solid solution of GaInN is not practical at present, as the nitrogen vacancy problems are exacerbated in this material. Future developments in nitrogen sources and/or growth techniques may change this situation.

The figure below shows the relationships of bandgap and lattice parameters for the hexagonal form of these materials. Data for the cubic forms of these materials is only available for GaN, thus it is not presented.

Work will also continue in the growth of the BGaN layers to promote the growth of cubic BN. Since there is a 20% lattice mismatch between BN and GaN, the proper growth of an intermediate layer will be critical in the production of high quality cBN films. An important part of that growth will be the use of XTEM to diagnose growth defects and other problems associated with the graded layer. The use of gas mixtures as already discussed above will also be an important part of the program to produce cubic BN.

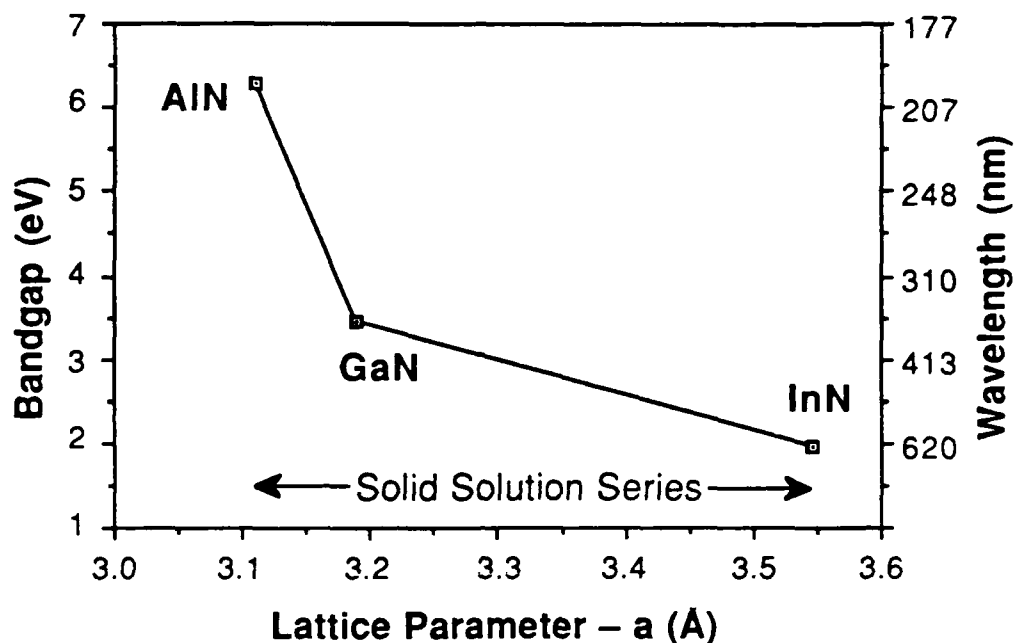


Figure 14. Diagram showing the relationship between lattice parameter and bandgap in the hexagonal structure solid solution series of GaN/AlN/InN.

5. Analysis System

The analytical system has been completed and has been used extensively in support of this program as well as a related SDIO program in diamond growth. This system consists of reverse view low energy electron diffraction, electron stimulated desorption, x-ray photoelectron spectroscopy and Auger electron spectroscopy. An ion gun is also present to permit depth profiling in conjunction with XPS and AES. It has an integral load lock system to allow samples to be loaded from atmosphere as well as connections to the diamond deposition system for *in situ* analysis of films. Connections between the MBE system and the analytical system will be made after all of the systems have been moved to Centennial Campus. This move is expected to occur in mid to late summer.

6. Related Activities

A paper entitled "Growth of cubic gallium nitride by modified molecular-beam epitaxy," by M. J. Paisley, Z. Sitar, J. B. Posthill, and R. F. Davis, was presented at the American Vacuum Society National

Symposium, in Atlanta, GA, in October, 1988, and subsequently appeared in the *Journal of Vacuum Science and Technology A*. [7]

Two papers have been submitted for presentation at the Tenth Molecular Beam Epitaxy Workshop to be held in Raleigh, NC in September, 1989. The titles are "Growth of AlN/InN solid solutions and AlN/GaN layered structures by gas source molecular beam epitaxy," by Z. Sitar, M. J. Paisley, and R. F. Davis; and "Growth of boron nitride films by gas source molecular beam epitaxy," by M. J. Paisley, Z. Sitar, and R. F. Davis.

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